Organometallic Compounds of the Lanthanides 182 [1]. Calcium and Neodymium Complexes Containing the dpp-BIAN Ligand System: Synthesis and Molecular Structure of $[(\text{dpp-BIAN})\text{CaI}(\text{THF})_2]_2$ and $[(\text{dpp-BIAN})\text{NdCl}(\text{THF})_2]_2$

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Oxydation of $(\text{dpp-BIAN})\text{Ca}(\text{THF})_4$ with 0.5 equiv. of I_2 in THF yields $[(\text{dpp-BIAN})\text{CaI}(\text{THF})_2]_2$ (**1**). A corresponding neodymium compound $[(\text{dpp-BIAN})\text{NdCl}(\text{THF})_2]_2$ (**2**) has been obtained by reaction of $(\text{dpp-BIAN})\text{Na}_2$ with $NdCl_3$ in THF. The X-ray single crystal structure analyses show **1** and **2** to be isostructural dimers containing octahedrally coordinated metal atoms bridged by the respective halides. The chelating dpp-BIAN ligand acts as a radical anion in the Ca^{2+} complex **1** and as a dianion in the Nd^{3+} complex **2**, respectively.

Key words: Neodymium, Calcium, Diimine Ligands, X-Ray Structure

Introduction

The metal ion-mediated condensation of acenaphthene quinone with aromatic amines producing acenaphthene-1,2-diimines (Ar-BIAN) has been reported by Matai [2] in 1960 and by Lixandru in 1967 [3]. With the exception of the synthesis of $(\text{BIAN})\text{PtCl}_2(\text{C}_2\text{H}_4)$ by Maresca *et al.* in 1975 [4], it took about 30 years until the particular suitability of Ar-BIAN systems as chelating ligands for metals has been recognized. The first results have been reported by van Asselt and Elsevier in the early 1990ies [5]. In the following years, numerous *d*-block metal complexes with different Ar-BIAN ligands have been described in more than 150 papers, and it turned out that many of the respective late transition metal complexes serve well as catalysts for a variety of organic transformations [6]. In contrast, investigations of the chemistry of *s*- and *p*-block element complexes with Ar-BIAN as ligand started only recently [7], and Ar-BIAN complexes of *f*-block metals are quite unknown until now.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) is the most widely used ligand of the Ar-BIAN series. One of the remarkable features of the dpp-BIAN ligand is its ability to adopt a variety of oxidation states. dpp-BIAN can be easily reduced by alkali metals to one-, two-, three-, and four-fold negatively charged anions yielding salts of the type $(\text{dpp-BIAN})^{n-}\text{M}_n^+(\text{L})_x$ (M = Li, Na; $n = 1-4$; L = Et_2O, THF) [7b]. Alkaline earth metals reduce dpp-BIAN only up to the stage of the dianion producing the monomeric complexes $(\text{dpp-BIAN})^{2-}\text{M}^{2+}(\text{L})_x$ (M = Mg, Ca, Sr, Ba; L = coordinating solvent) [7c, 7i].

Because the alkaline earth elements and the metals of the lanthanide series show certain similarities, the latter may be called "pseudo-alkaline earth metals". First of all, the elements of these two groups represent electropositive metals with values of their electronegativity close to 1.1. However, whereas the ionic radii of the alkaline earth elements increase from Mg to Ba, the ionic radii of the lanthanide metals decrease with increasing atomic number. The ionic radii of the early lanthanide metal ions in the common oxidation state Ln^{3+} range from 1.032 Å for La^{3+} to 0.983 Å for Nd^{3+} and are close to the ionic radius of Ca^{2+} (1.00 Å) [8]. In this context it has been observed that complexes of

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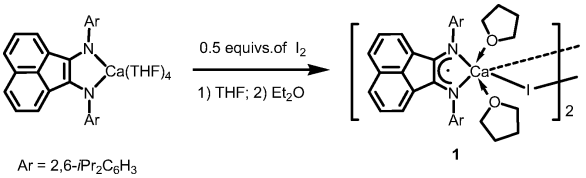
Ca^{2+} and Yb^{2+} ions with one and the same ligand show almost identical structural parameters [9]. This fact has been the motivation for our studies of dpp-BIAN complexes of the early lanthanides. In this paper we report on the synthesis of the first dpp-BIAN neodymium complex and on the result of a comparison of its molecular structure with that of an analogous calcium complex using single crystal X-ray structure analysis.

Results and Discussion

*Synthesis of [(dpp-BIAN)CaI(THF)$_2$]$_2$ (**1**) and [(dpp-BIAN)NdCl(THF)$_2$]$_2$ (**2**)*

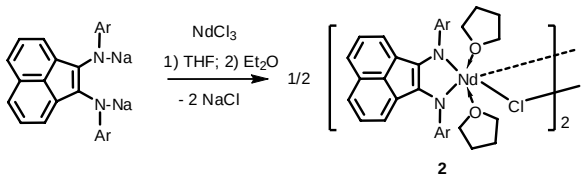
Addition of 0.5 equiv. of iodine to a solution of (dpp-BIAN)Ca(THF)$_4$ [7c] in THF causes an immediate change in the color of the solution from green-brown to cherry-red, indicative of the oxidation of the dianion $[(\text{dpp-BIAN})]^{2-}$ in the starting calcium compound to the radical-anion $[(\text{dpp-BIAN})]^{\bullet-}$ in the complex [(dpp-BIAN)CaI(THF)$_2$]$_2$ (**1**) formed (Scheme 1). The deep red crystals of the dimeric compound **1**, isolated from diethyl ether in a yield of 53 %, melt without decomposition between 195 and 197 °C and are sensitive against moisture and air. The ESR spectrum of **1** recorded in toluene at 293 K shows a quintet (g = 2.00333) with coupling of the unpaired electron to the ^{14}N, ^{1}H and ^{127}I nuclei ($A(^{14}\text{N})$ = 0.44 (2 N); $A(^{127}\text{I})$ = 0.05 (1 I); $A(^{1}\text{H})$ = 0.10 (4 H) mT).



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 1. Synthesis of **1**.

$NdCl_3$ reacts with the green disodium salt (dpp-BIAN)Na$_2$ [7b] in THF with formation of the complex [(dpp-BIAN)NdCl(THF)$_2$]$_2$ (**2**) (Scheme 2). The reaction is connected with a change of the color of the solution from green to blue. Compound **2** crystallizes from diethyl ether as deep blue, nearly black crystals in a yield of 57 %. As it is the case with the blue aluminum [10] and gallium complexes [11], the color of the crystals of **2** indicates the existence of the dpp-BIAN ligand in its dianionic form. The air and moisture sensitive compound **2** melts without decomposition between 210 and 215 °C. Besides diethyl ether and THF, the complex is soluble in aromatic hydrocarbons.



Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 2. Synthesis of **2**.

Compounds **1** and **2** are paramagnetic, the calcium derivative due to the presence of the radical-anionic dpp-BIAN ligand and the neodymium complex due to the paramagnetism of the Nd^{3+} ion. For this reason, no NMR spectroscopic measurements were carried out. The complexes have been characterized by elemental analysis, IR spectroscopic investigations, and by determination of their molecular structure.

*Molecular structures of [(dpp-BIAN)CaI(THF)$_2$]$_2$ (**1**) and [(dpp-BIAN)NdCl(THF)$_2$]$_2$ (**2**)*

Crystals of **1** and **2** suitable for single crystal X-ray diffraction were obtained by slow evaporation of ethereal solutions of the compounds. Both complexes are isostructural in the crystalline state. They form dimers bridged by I and Cl atoms, respectively, with crystallographic inversion centers located at the center of the line between the metal atoms (Figs. 1 and 2). The calcium and neodymium atoms are in the center of an octahedral environment formed by the two nitrogen atoms of the dpp-BIAN ligand, the oxygen atoms of the two coordinated THF molecules and the respective two bridging halogen atoms. One of the THF ligands is in a position *trans* to one of the nitrogen atoms of the dpp-BIAN ligand, the other one is in a *trans* position to one of the bridging halogen atoms. The Ca-O distances in **1** (O(1)-Ca 2.405(3), O(2)-Ca 2.399(3) Å) are somewhat shorter than the Nd-O distances in **2** (O(1)-Nd 2.470(4), O(2)-Nd 2.525(3) Å). On the other hand, the Ca-N distances in **1** (N(1)-Ca 2.467(4), N(2)-Ca 2.452(4) Å) are remarkably longer than the Nd-N distances in **2** (N(1)-Nd 2.345(4), N(2)-Nd 2.303(4) Å). This fact reflects a stronger bonding of the neodymium ion to the dpp-BIAN dianion in **2** as compared to the bonding of the calcium ion to the radical-anionic dpp-BIAN ligand in **1**. For comparison, the Ca-N distances in (dpp-BIAN)Ca(THF)$_4$ containing dpp-BIAN dianions are 2.396(2) and 2.382(2) Å [7c].

The X-ray crystallographic data confirm the "reduction state" of the dpp-BIAN ligand in **1** and **2**. The changes in the population of the LUMO on going

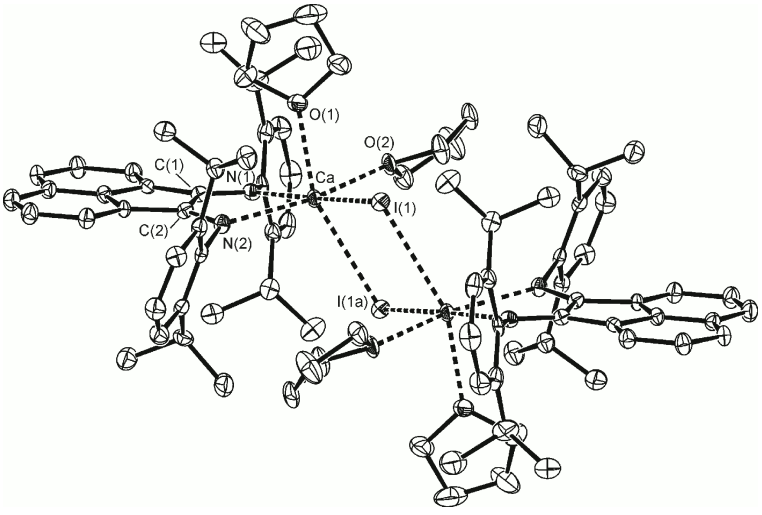


Fig. 1. ORTEP [12] presentation of the molecular structure of **1** (30 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): C(1)-N(1) 1.340(6), C(2)-N(2) 1.332(5), C(1)-C(2) 1.456(6), N(1)-Ca 2.467(4), N(2)-Ca 2.452(4), O(1)-Ca 2.405(3), O(2)-Ca 2.399(3), Ca-I(1) 3.2079(11), Ca-I(1a) 3.1657(11); O(2)-Ca-O(1) 84.21(13), O(2)-Ca-N(2) 163.12(14), O(1)-Ca-N(2) 91.77(13), O(2)-Ca-N(1) 91.32(13), O(1)-Ca-N(1) 89.36(12), N(2)-Ca-N(1) 72.21(14), I(1)-Ca-I(1a) 79.34(3).

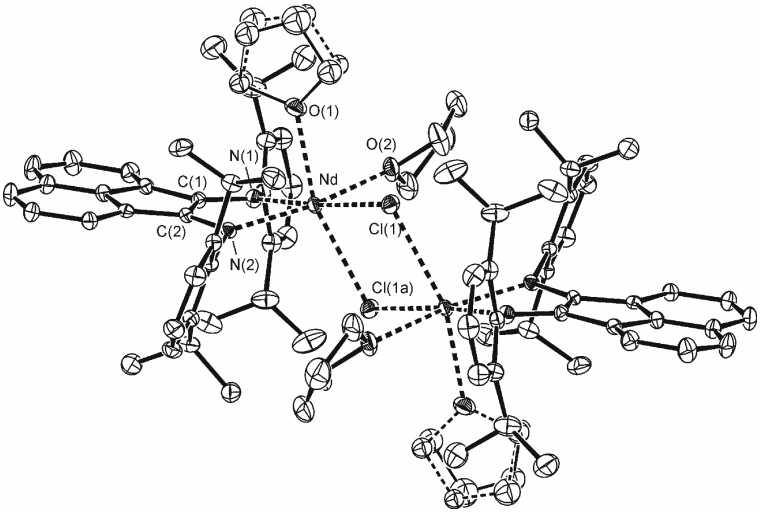


Fig. 2. ORTEP [12] presentation of the molecular structure of **2** (30 % probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): C(1)-N(1) 1.396(6), C(2)-N(2) 1.396(6), C(1)-C(2) 1.388(6), N(1)-Nd 2.345(4), N(2)-Nd 2.303(4), O(1)-Nd 2.470(4), O(2)-Nd 2.525(3), Nd-Cl(1a) 2.8184(14), Nd-Cl(1) 2.8974(13); O(2)-Nd-O(1) 88.01(12), O(2)-Nd-N(2) 162.67(13), O(1)-Nd-N(2) 89.63(13), O(2)-Nd-N(1) 88.31(13), O(1)-Nd-N(1) 91.35(13), N(2)-Nd-N(1) 74.58(13), Cl(1)-Nd-Cl(1a) 75.27(4).

from neutral dpp-BIAN to its radical anion and further to its dianion suggest a progressive shortening of the central C(1)–C(2) bond associated with an increasing elongation of the C(1)–N(1) and C(2)–N(2) distances. Our results agree with this expectation showing that in **1** containing the dpp-BIAN radical anion, the C(1)–N(1) and C(2)–N(2) bonds (1.340(6), 1.332(5) Å) are longer than in free dpp-BIAN (both 1.282(4) Å) [13], but shorter than in the dpp-BIAN dianion in the complex (dpp-BIAN)Ca(THF)$_4$ (1.391(3) and 1.402(3) Å) [7c]. The C(1)-N(1) and C(2)-N(2) distances in **2** (1.396(6) and 1.396(6) Å) agree well with those in (dpp-BIAN)Ca(THF)$_4$, thus confirming the dianionic character of the dpp-BIAN ligand in **2**.

Experimental Section

All manipulations were carried out in vacuum using standard Schlenk techniques or in an inert atmosphere. The solvents THF and Et_2O were distilled from sodium/benzophenone prior to use. The IR spectra were recorded using a Bruker Vertex 70 instrument. Elemental analyses were carried out using a Perkin-Elmer Series II CHNS/O Analyzer 2400. dpp-BIAN [14] was prepared according to the published procedure.

*[(dpp-BIAN)CaI(THF)$_2$]$_2$ (**1**)*

According to the procedure described recently [7c], calcium metal granules (5.5 g, 137 mmol) in THF (30 mL) were activated by CH_2I_2 (0.8 g, 2.98 mmol) and then treated

Table 1. Parameters of the single crystals, data collection and structure refinement of **1** and **2**.

	1	**2**
Empirical formula	$C_{96}H_{132}Ca_2I_2N_4O_6$	$C_{96}H_{132}Cl_2N_4Nd_2O_6$
Formula wt., g mol^{-1}	1772.02	1797.44
Crystal size, mm^3	$0.12 \times 0.06 \times 0.05$	$0.56 \times 0.50 \times 0.33$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Z	2	2
a, Å	12.1519(17)	15.032(5)
b, Å	18.293(3)	18.056(5)
c, Å	21.451(4)	16.962(5)
β, deg	100.860(13)	98.404(5)
V, Å^3	4682.9(13)	4554(2)
D_{calcd}, g cm^{-3}	1.257	1.311
Absorp. coeff., mm^{-1}	0.833	1.239
Transmission min/max	0.921/0.840	0.74120/0.27834
$F(000)$, e	1860	1876
2θ range for data collection, deg	$2.95 \leq \theta \leq 28.75$	$1.66 \leq \theta \leq 25.00$
hkl-Range	$-15 \leq h \leq 15$	$-13 \leq h \leq 17$
	$-24 \leq k \leq 22$	$-21 \leq k \leq 20$
	$-25 \leq l \leq 27$	$-20 \leq l \leq 18$
Reflections, collected	24316	28237
Reflections, unique	10292	8012
R_{int}	0.082	0.107
Data/restraints/param.	10292/0/506	8012/19/501
Goodness-of-Fit (F^2)	0.889	1.043
$R1/wR2$ $[I \geq 2\sigma(I)]$	0.062/0.103	0.050/0.122
$R1/wR2$ (all data)	0.155/0.118	0.066/0.139
Largest diff. peak and hole, e Å^{-3}	0.87/−0.77	1.55/−1.26

with dpp-BIAN (0.5 g, 1 mmol) in THF (50 mL). After stirring the mixture under reflux for 1 h, it was cooled down to r. t. and the solution was decanted from excess Ca metal. To the separated solution containing (dpp-BIAN)Ca(THF)$_4$, iodine (0.13 g, 0.5 mmol) was added with stirring. The color of the reaction mixture changed immediately from green-brown to cherry-red. After 1 h, the solvent was removed in vacuum. The remaining crude product was dissolved in diethyl ether (45 mL) and the solution was filtered off. Slow evaporation of the ether resulted in the precipitation of deep red crystals of **1** (0.47 g, 53 %). M. p. 195 – 197 °C. – IR (Nujol): ν = 1668 (m), 1640 (m), 1593 (m), 1512 (s), 1410 (s), 1314 (m), 1276 (w), 1252 (m), 1221 (w), 1185 (s), 1119 (m), 1076 (w), 1030 (s), 939 (w), 926 (m), 877 (m), 844 (s), 836 (m), 821 (m), 803 (w), 787 (m), 777 (m), 759 (m), 751 (s) cm^{-1}. – $C_{88}H_{112}Ca_2I_2N_4O_4 \times 2$ Et_2O (1772.10): calcd. C 65.07, H 7.51; found C 64.85, H 7.38.

*[(dpp-BIAN)NdCl(THF)$_2$]$_2$ (**2**)*

According to the procedure described recently [7b], dpp-BIAN (0.56 g, 1.12 mmol) in THF (30 mL) was added to an ampoule containing a piece of sodium (52 mg, 2.3 mmol) and the mixture was stirred at r. t. for 4 h. To the decanted green solution of (dpp-BIAN)Na$_2$, $NdCl_3(THF)_{2.1}$ (0.45 g, 1.1 mmol) was added. With precipitation of NaCl, the color of the reaction mixture changed from green to blue. The mixture was stirred for 1 h at ambient temperature followed by evaporation of the solvent in vacuum. The residue was dissolved in Et_2O (50 mL) and the deep blue solution was filtered off from insoluble NaCl. Slow evaporation of the solvent resulted in the precipitation of deep blue crystals of **2** (0.56 g, 57 %). M. p. 210 – 215 °C. – IR (Nujol): ν = 1919(w), 1857(w), 1791(w), 1669(w), 1612(m), 1582(s), 1305(m), 1253(m), 1184(m), 1122(m), 1038(w), 916(s), 857(m), 813(m), 797(m), 767(s), 758(s), 749(s), 696(m), 683(m), 625(s), 600(w), 541(m), 512(m) cm^{-1}. – $C_{88}H_{112}Cl_2N_4Nd_2O_4 \times 2$ Et_2O (1797.51): calcd. C 64.15, H 7.40; found C 64.79, H 7.45.

Crystal structure determination

Crystals suitable for X-ray diffraction were obtained by crystallization of **1** and **2** from diethyl ether. The data of **1** were collected using an Xcalibur S Sapphire diffractometer (Oxford Diffraction) at 150 K, the data of **2** using a Siemens SMART CCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71070 Å) and ω scans at 173 K. The structures were solved by Direct Methods using SIR97 [15] or SIR2004 [16] and were refined with SHELXL-97 [17] on F^2 using all reflections. All non-hydrogen atoms were refined anisotropically and the carbon-bound hydrogen atoms were placed in calculated positions using a riding model. For **2**, SADABS [18] was used to perform area-detector scaling and absorption corrections. The important parameters of the single crystals, the data collection and the refinement of the structures are listed in Table 1.

CCDC 641588 (**1**) and 641589 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] Part 181: H. Schumann, D. M. M. Freckmann, S. Schutte, S. Dechert, M. Hummert, *Z. Anorg. Allg. Chem.* **2007**, *633*, 888.

[2] I. Matei, T. Lixandru, E. Comanita, *Acad. Rep. Populare Romine, Filiala Iasi, Studii Cercetari Stiint. Chim* **1960**, *11*, 281.

[3] I. Matei, T. Lixandru, *Buletinul Institutului Politehnic din Iasi* **1967**, *13*, 245.
[4] L. Maresca, G. Natile, L. Cattalini, *Inorg. Chim. Acta* **1975**, *14*, 79.
[5] a) R. van Asselt, E. E. C. G. Gielens, R. E. Rulke, C. J. Elsevier, *J. Chem. Soc., Chem. Commun*. **1993**, 1203; b) R. van Asselt, E. E. C. G. Gielens, R. E. Rulke, K. Vrieze, C. J. Elsevier, *J. Am. Chem. Soc*. **1994**, *116*, 977; c) R. van Asselt, E. Rijnberg, C. J. Elsevier, *Organometallics* **1994**, *13*, 706; d) R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, *Inorg. Chem*. **1994**, *33*, 1521; e) R. van Asselt, C. J. Elsevier, *Organometallics* **1994**, *13*, 1972; f) R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Rec. Trav. Chim. Pays-Bas* **1994**, *113*, 88.
[6] a) R. van Asselt, C. J. Elsevier, *Tetrahedron* **1994**, *50*, 323; b) S. Tollari, S. Cenini, F. Ragaini, L. Cassar, *J. Chem. Soc., Chem. Commun*. **1994**, 1741; c) L. K. Johnson, Ch. M. Killian, M. Brookhart, *J. Am. Chem. Soc*. **1995**, *117*, 6414; d) S. Cenini, F. Ragaini, St. Tollari, D. Paone, *J. Am. Chem. Soc*. **1996**, *118*, 11964; e) J. H. Groen, J. G. P. Delis, P. W. N. M. van Leeuwen, K. Vrieze, *Organometallics* **1997**, *16*, 68; f) R. van Belzen, H. Hoffmann, C. J. Elsevier, *Angew. Chem*. **1997**, *109*, 1833; *Angew. Chem. Int. Ed*. **1997**, *36*, 1743; g) R. van Belzen, R. A. Klein, H. Kooijman, N. Veldman, A. L. Spek, C. J. Elsevier, *Organometallics* **1998**, *17*, 1812; h) E. Shirakawa, H. Yoshida, Y. Nakao, T. Hiyama, *J. Am. Chem. Soc*. **1999**, *121*, 4290; i) M. W. van Laren, C. J. Elsevier, *Angew. Chem*. **1999**, *111*, 3926; *Angew. Chem. Int. Ed*. **1999**, *38*, 3715; j) F. Ragaini, S. Cenini, St. Tollari, G. Tummolillo, R. Beltrami, *Organometallics* **1999**, *18*, 928; k) F. Ragaini, P. Sportiello, S. Cenini, *J. Organomet. Chem*. **1999**, *577*, 283; l) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev*. **2000**, *100*, 1169; m) D. B. Llewellyn, D. Adamson, B. A. Arndtsen, *Org. Lett*. **2000**, *2*, 4165; n) F. Ragaini, S. Cenini, E. Borsani, M. Dompé, E. Gallo, *Organometallics* **2001**, *20*, 3390; o) G. A. Grasa, A. C. Hillier, S. P. Nolan, *Org. Lett*. **2001**, *3*, 1077; p) G. A. Grasa, R. Singh, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem*. **2003**, *687*, 269.
[7] a) H. A. Jenkins, C. L. Dumaresque, D. Vidovic, J. A. C. Clyburne, *Can. J. Chem*. **2002**, *80*, 1398; b) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, *Angew. Chem*. **2003**, *115*, 3416; *Angew. Chem. Int. Ed*. **2003**, *42*, 3294; c) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, H. Schumann, *Eur. J. Inorg. Chem*. **2003**, 3336; d) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, V. K. Cherkasov, G. K. Fukin, M. A. Lopatin, *Eur. J. Inorg. Chem*. **2004**, 388; e) R. J. Baker, C. Jones, M. Kloth and D. P. Mills, *New J. Chem*. **2004**, *28*, 207; f) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, N. M. Khvoinova, A. Yu. Baurin, S. Dechert, M. Hummert, H. Schumann, *Organometallics* **2004**, *23*, 3714; g) I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, M. P. Bubnov, *Inorg. Chem*. **2004**, *43*, 7807; h) I. L. Fedushkin, V. A. Chudakova, A. A. Skatova, N. M. Khvoinova, Yu. A. Kurskii, T. A. Glukhova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Z. Anorg. Allg. Chem*. **2004**, *630*, 501; i) I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, G. K. Fukin, *Chem. Eur. J*. **2005**, *11*, 5749; j) H. Schumann, M. Hummert, A. N. Lukoyanov, I. L. Fedushkin, *Organometallics* **2005**, *24*, 3891; k) P. J. Bailey, C. M. Dick, S. Fabre, S. Parsons, L. J. Yellowlees, *Dalton Trans*. **2006**, 1602; l) G. Reeske, C. R. Hoberg, N. J. Hill, A. H. Cowley, *J. Am. Chem. Soc*. **2006**, *128*, 2800; m) N. J. Hill, G. Reeske, J. A. Moore, A. H. Cowley, *Dalton Trans*. **2006**, 4838.
[8] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.
[9] a) R. A. Williams, T. P. Hanusa, J. C. Huffman, *Organometallics* **1990**, *9*, 1128; b) I. L. Fedushkin, T. V. Petrovskaya, M. N. Bochkarev, S. Dechert, H. Schumann, *Angew. Chem*. **2001**, *113*, 2540; *Angew. Chem. Int. Ed*. **2001**, *40*, 2474; c) F. Weber, H. Sitzmann, M. Schultz, C. D. Sofield, R. A. Anderson, *Organometallics* **2002**, *21*, 3139; d) H. Schumann, S. Schutte, H. J. Kroth, D. Lenz, *Angew. Chem. Int. Ed.* **2004**, *43*, 6208.
[10] A. N. Lukoyanov, I. L. Fedushkin, H. Schumann, M. Hummert, *Z. Anorg. Allg. Chem*. **2006**, *632*, 1471.
[11] A. N. Lukoyanov, S. Y. Ketkov, M. Hummert, H. Schumann, *Chem. Eur. J.*, in press.
[12] A. L. Spek, PLATON, A. Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2000**. See also: A. L. Spek, *J. Appl. Cryst*. **2003**, *36*, 7 – 13.
[13] I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bul. Int. Ed*. **2004**, *53*, 2744.
[14] A. A. Paulovicova, U. El-Ayaan, K. Shibayama, T. Morita, Y. Fukuda, *Eur. J. Inorg. Chem*. **2001**, 2641.
[15] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97, *J. Appl. Crystallogr*. **1999**, *32*, 115 – 119.
[16] M. C. Burla, R. Caliandro, M. Cavalli, B. Carrozzini, G. L. Cascarano, L. de Caro, C. Giacovazzo, G. Polidori, R. Spagna, SIR2004, *J. Appl. Cryst*. **2005**, *38*, 381 – 388.
[17] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
[18] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1997**.